Bandgap Modulation of Boron Nitride-doped Graphene

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Since its discovery, graphene has shown to exhibit remarkable electronic properties [1]. Numerous techniques have been devised to create high-performance devices by manipulating the bandgap in order to enhance their semiconducting properties [2].

Doping has proven to be one of the most effective methods for bandgap engineering. Experimental and theoretical studies on graphene doping show the possibility of making p-type and n-type semiconducting graphene by substituting C atoms. Boron and nitrogen have been specifically studied during the last years due to the interesting insulating behavior of h-BN. Boron, nitrogen, and carbon can be atomically mixed to form various semiconducting, hexagonal, layered structures. Experimental and theoretical studies have indicated that BNC nanostructures show semiconducting properties with small bandgaps [2,3]. Low concentrations of borazine rings within the graphene structure can modify graphene's electronic properties to form a 2D semiconductor material with homogeneous patterns [4,5]. The intercalation of hexagonal BN (h-BN) within the graphene lattice has already been successfully achieved, however, segregation of both materials has been the main issue. Recent research has demonstrated that incorporating borazine-like molecules with carbon structures into graphene can result in reduced segregation of h-BN domains [5,6]. Herrera Reinoza et al. demonstrated a notable example by depositing hexamethylborazine onto Ir(111), which yielded numerous boron-nitrogen-carbon (BNC) domains exhibiting low BN segregation and an estimated bandgap ranging between 1.4 and 1.6 eV [6].

To grow our boron nitride-doped graphene nanomaterial we first synthesized graphene via chemical vapor deposition (CVD) by cyclic exposures to 10^{-5} mbar of ethylene for 10 minutes with subsequent annealing at 1100 K for 10 minutes. We have successfully doped our graphene by exposing it to hexamethylborazine right after the 3rd cycle of graphene synthesis. Auger electron spectroscopy demonstrated the presence of B, C and N in the sample. A bandgap was opened on our BN-doped graphene, forming a semiconductor material.

[1] Geim, A. K. & Novoselov, K. S. The rise of graphene. *Nat Mater* **6**, 183–191 (2007).
[2] Ci, L. *et al.* Atomic layers of hybridized boron nitride and graphene domains. **9**, 430–435 (2010).
[3] Caputo, L., Nguyen, V.-H. & Charlier, J.-C. First-principles study of the structural and electronic properties of BN-ring doped graphene. *Phys Rev Mater* **6**, 114001 (2022).
[4] Gao, L., Guest, J. R. & Guisinger, N. P. Epitaxial graphene on Cu(111). *Nano Lett* **10**, 3512–3516 (2010).
[5] Sánchez-Sánchez, C. *et al.* On-Surface Synthesis of BN-Substituted Heteroaromatic Networks. *ACS Nano* **9**, 9228–9235 (2015).
[6] Herrera-Reinoza, N., Dos Santos, A. C., De Lima, L. H., Landers, R. & De Siervo, A. Atomically Precise Bottom-Up Synthesis of h-BNC: Graphene Doped with h-BN Nanoclusters. *Chemistry of Materials* **33**, 2871–2882 (2021).